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(54) Title: INK-JET PRINTABLE SUBSTRATE WITH ANTICURL LAYER

(57) Abstract

The present invention is directed to improved substrates containing an anticurl layer, which minimizes the tendency of the substrate to curl. The present invention also relates to improved substrates comprising an anticurl layer on a back surface of the substrate and a colorant-receiving composition of the front surface of the substrate. The colorant-receiving composition provides superior print quality and colorant stability to the substrate. The improved substrates of the present invention enable the production of superior print quality while providing enhanced lightfastness for colorants and colorant compositions against radiation including radiation in the visible wavelength range.

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INK-JET PRINTABLE SUBSTRATE WITH ANTICURL LAYER

Technical Field

The present invention relates to improved substrates containing an anticurl layer. The improved substrates, according to the present invention, are capable of improving print quality and contributing to the light stabilization of a colorant on the substrate, when the colorant is exposed to electromagnetic radiation. Further, the improved substrates of the present invention provide superior print quality and colorant stabilization with minimal curling. The improved substrates enable the production of a printed substrate having superior print quality and minimal curl compared to conventional substrates.

Background of the Invention

A major problem with colorants is that they tend to fade when exposed to electromagnetic radiation such as sunlight or artificial light and the like. It is believed that most of the fading of colorants when exposed to light is due to photodegradation mechanisms. These degradation mechanisms include oxidation or reduction of the colorants depending upon the environmental conditions in which the colorant is placed. Fading of a colorant also depends upon the substrate upon which they reside.

Product analysis of stable photoproducts and intermediates has revealed several important modes of photodecomposition. These include electron ejection from the colorant, reaction with ground-state or excited singlet state oxygen, cleavage of the central carbon-phenyl ring bonds to form amino substituted benzophenones, such as triphenylmethane dyes, reduction to form the colorless leuco dyes and electron or hydrogen atom abstraction to form radical intermediates.

Various factors such as temperature, humidity, gaseous reactants, including O_2, O_3, SO_2, and NO_2, and water soluble, nonvolatile photodegradation products have been shown to influence fading of colorants. The factors that effect colorant fading appear to exhibit a certain amount of interdependence. It is due to this complex behavior that observations for the fading of a particular colorant on a particular substrate cannot be applied to colorants and substrates in general.

Under conditions of constant temperature it has been observed that an increase in the relative humidity of the atmosphere increases the fading of a colorant for a variety of colorant-substrate systems (e.g., McLaren, K., *J. Soc. Dyers Colour*, 1956, 72, 527). For example, as the relative humidity of the atmosphere increases, a fiber may swell because the moisture content of the fiber increases. This aids diffusion of gaseous reactants through the substrate structure.

The ability of a light source to cause photochemical change in a colorant is also dependent upon the spectral distribution of the light source, in particular the proportion of radiation of wavelengths most effective in causing a change in the colorant and the quantum yield of colorant degradation as a function of wavelength. On the basis of photochemical principles, it would be expected that light of higher energy (short wavelengths) would be more effective at causing fading than light of lower energy (long wavelengths). Studies have revealed that this is not always the case. Over 100 colorants of

different classes were studied and found that generally the most unstable were faded more efficiently by visible light while those of higher lightfastness were degraded mainly by ultraviolet light (McLaren, K., J. *Soc. Dyers Colour*, 1956, 72, 86).

The influence of a substrate on colorant stability can be extremely important. Colorant fading may be retarded or promoted by one or more chemical groups within the substrate. Such a group can be a ground-state species or an excited-state species. The porosity of the substrate is also an important factor in colorant stability. A high porosity can promote fading of a colorant by facilitating penetration of moisture and gaseous reactants into the substrate. A substrate may also act as a protective agent by screening the colorant from light of wavelengths capable of causing degradation.

The purity of the substrate is also an important consideration whenever the photochemistry of dyed technical polymers is considered. For example, technical-grade cotton, viscose rayon, polyethylene, polypropylene, and polyisoprene are known to contain carbonyl group impurities. These impurities absorb light of wavelengths greater than 300 nm, which are present in sunlight, and so, excitation of these impurities may lead to reactive species capable of causing colorant fading (van Beek, H.C.A., *Col. Res. Appl.*, 1983, 8(3), 176).

Conventional print substrates result in acceptable print quality; however, certain print defects still exist resulting in less than desirable print quality. Printing defects, such as "feathering" and "wicking", undesirably spread the colorant or colorant composition beyond the desired print pattern and/or pull the colorant or colorant composition into the print substrate. The result is a smeared print pattern, wherein a substantial portion of the colorant or colorant composition migrates below and beyond the intended area of the print substrate.

In order to improve the print quality and colorant stability of print substrates, one or more coatings are applied to the colorant-receiving surface of the substrate. Typically, the coatings contain anti-wicking and anti-feathering components, as well as, colorant stabilizers in a solvent such as water. As the solvent is removed from the coating, the substrate has a tendency to curl toward the coated surface. For instance, a polyethylene/paper/polyethylene base substrate coated with a coating on the colorant-receiving surface of the substrate will have a tendency to curl toward the colorant-receiving surface (i.e., when the colorant-receiving coating is facing upward, the edges of the substrate have a tendency to curl upward). Various attempts have been made in the art to minimize the tendency of print substrates to curl. However, these attempts have not been fully successful to date.

Therefore, there exists a need for improved substrates which possess superior substrate stability. There is also a need in the art for improved substrates having anticurl properties, which are capable of providing superior print quality, with minimal print defects, such as "feathering" and "wicking" of a colorant composition. There is a further need in the art for improved substrates having anticurl properties, which are capable of minimizing print defects while providing significant light stability from the effects of both sunlight and artificial light for a wide variety of colorants and colorant compositions.

Summary of the Invention

The present invention addresses the needs described above by providing an improved substrate for colorants and colorant compositions. The improved substrates possess an anticurl layer, which minimizes the tendency of the substrate to curl. The improved substrates of the present invention enable the production of superior print quality while providing enhanced lightfastness for colorants and colorant compositions

against radiation including radiation in the visible wavelength range.

The present invention also relates to improved substrates comprising an anticurl layer on a back surface of the substrate and a colorant-receiving composition of the front surface of the substrate. The colorant-receiving composition provides superior print quality and colorant stability to the substrate.

The present invention is also directed to improved substrates comprising an anticurl layer on a back surface of the substrate and a colorant or colorant composition on a face surface of the substrate. The colorant or colorant composition may contain one or more colorant stabilizers. Desirably, the colorant stabilizers are represented by porphines having an extremely short triplet state lifetime.

Unsurpassed substrate stability is achieved by combining the anticurl layer of the present invention with a variety of print substrates. Further, unsurpassed print quality, print vibrance, colorant stability, and substrate stability is achieved by combining the aforementioned improved substrates and colorant compositions. These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

Detailed Description of the Invention

The present invention is directed to improved substrates having an anticurl layer thereon. The improved substrates possess superior substrate stability, while enabling the production of superior print quality and providing enhanced lightfastness for colorants and colorant compositions against radiation including radiation in the visible wavelength range. The improved substrates are suitable for use with any colorant or colorant composition, and especially colorant or colorant compositions containing one or more light stabilizers.

The improved substrate of the present invention comprises a base layer coated with an anticurl layer. The anticurl layer contains one or more polymeric binders and optionally one or more sugars and/or starches. The base layer, to which the anticurl layer is applied, includes, but is not limited to, paper, wood, a wood product or composite, woven fabric, nonwoven fabric, textile, plastic, glass, metal, or any other substrate capable of maintaining the binder composition thereon. Examples of suitable substrates are disclosed in U.S. Patent Application Serial No. 08/843,410, assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference.

The base layer may comprise one or more of the above-mentioned layers. In one embodiment of the present invention, the base layer is a coated or uncoated fiber-containing substrate such as Photoglossy Base, Presentation Matte Photobase, and High Quality Matte papers and Wetstrength Media; a film such as White Opaque Films (e.g. KIMDURA®, K-C), Clears Films (e.g. MELINEX®, ICI) Backlit Films, and Vinyl; or a nonwoven such as TYVEK®. Desirably, the base layer is a coated or uncoated paper. More desirably, the base layer is a coated paper comprising a cellulose sheet coated with a polymeric film, such as polyethylene, on both sides of the paper. One particularly suitable coated paper comprising polyethylene/paper/polyethylene is available from Jen-coat Papers.

When the base layer is a coated paper comprising a cellulose sheet coated with a polyethylene film on both sides of the paper, one or more treatments may be used to improve the wettability of the base layer with subsequently applied water-based coatings. One such treatment is a corona discharge treatment of the base layer. Another treatment is a gel coating applied to one or both sides of the base layer. Particularly suitable base layers having one or more of the above treatments are commercially available papers from Schoeller

Paper, designated SN1435 and SN1436. SN1435 is a 7.3 mil paper having a satin finish and a face side gel coating. SN1436 is a 6.2 mil paper having a high gloss finish, a face side gel coating and a back side gel coat.

The anticurl layer may contain one or more polymeric binders. Suitable binder materials include, but are not limited to, naturally-occurring polymers, synthetically-modified naturally-occurring polymers or synthetic polymers as exemplified in *Water-Soluble Polymers*, C. L. McCormick, J. Bock, and D. N. Schulz, in Vol. 17, Encyclopedia of Polymer Science and Engineering, John Wiley and Sons, Publishers (1989), pgs. 730-84. Desirably, the binder composition contains one or more of the following polymers: polyvinylpyrrolidone (PVP), polyvinylalcohol (PVOH), polyhydroxyethyl acrylate, polyhydroxyethyl methacrylate, polyacrylamide, polymethacrylamide, polyethylene glycol, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, polyacrylic acid and polyacrylic acid salts, polymethacrylic acid and polymethacrylic acid salts, polyvinylsulfonate and polyvinylsulfonate salts, poly-2-acrylamido-2-methylpropanesulfonic acid and poly-2-acrylamido-2-methylpropanesulfonic acid salts, polyacryloxy-trimethylammonium chloride, polymethacryloxytrimethyl-ammonium chloride, and polydiallyldimethylammonium chloride. In one embodiment of the present invention, the binder composition contains hydroxypropyl cellulose, carboxymethyl cellulose or a combination thereof.

The anticurl layer may also contain one or more sugars and/or starches. Desirably, the one or more sugars and/or starches comprise one or more dextrins. Suitable dextrins include linear dextrins and cyclodextrins. Suitable linear dextrins include, but are not limited to, linear dextrin available from Archer Daniel Midland Corporation, Clinton, Iowa, under the tradename CLINTON 926™. Suitable cyclodextrins

include, but are not limited to, α-cyclodextrin, β-cyclodextrin, γ-cyclodextrin, δ-cyclodextrin, hydroxypropyl β-cyclodextrin, hydroxyethyl β-cyclodextrin, hydroxyethyl α cyclodextrin, carboxymethyl α cyclodextrin, carboxymethyl β cyclodextrin, carboxymethyl γ cyclodextrin, octyl succinated α cyclodextrin, octyl succinated β cyclodextrin, octyl succinated γ cyclodextrin and sulfated β cyclodextrin and sulfated γ-cyclodextrin (Cerestar USA Incorporated, Hammond, Indiana). Desirably, the anticurl layer contains a linear dextrin, β-cyclodextrin (β-CD), hydroxypropyl β-cyclodextrin (hp-β-CD), or a combination thereof.

In one embodiment of the present invention, the anticurl layer contains from about 100 to about 10 weight percent polymeric binder and from about 0 to about 90 weight percent dextrin. More desirably, the binder composition contains from about 75 to about 25 weight percent polymeric binder and from about 25 to about 75 weight percent dextrin. Most desirably, the binder composition contains from about 65 to about 25 weight percent polymeric binder and from about 35 to about 75 weight percent dextrin.

In addition to the polymeric binder and the cyclodextrin, the anticurl layer of the present invention may also contain additional components. Examples of such additional components include, but are not limited to, charge carriers; stabilizers against thermal oxidation; viscoelastic properties modifiers; cross-linking agents; plasticizers; charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; fillers such as calcium carbonate, clay and talc; surfactants; detackifiers; chelating agents; and TINUVIN® compounds; among other additives used by those having ordinary skill in the art. Charge carriers are well known to those having ordinary skill in the art and typically are polymer-coated metal particles. Desirable surfactants include,

but are not limited to, C_{12} to C_{18} surfactants such as cetyl trimethyl ammonium chloride and carboxymethylamylose, and other surfactants such as Triton X-100 and SURFYNOL® 420. TINUVIN® compounds are a class of compounds produced by Ciba-Geigy Corporation, which includes benzophenones, benzotriazoles and hindered amines. Desirable TINUVIN® compounds include, but are not limited to, 2-(2'-hydroxy-3'-*sec*-butyl-5'-*tert*-butylphenyl)-benzo-triazole, poly-(N-ß-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate and 2-(2'-hydroxy-3',5'-di*tert*butylphenyl)-5-chloro-benzotriazole. The identities and amounts of such additional components in the colored composition are well known to one of ordinary skill in the art. Typically, one or more of the above additives are present in the anticurl layer in an amount of from about 1 to 14 weight percent based on the total weight of the anticurl layer.

In one embodiment of the present invention, the anticurl layer contains filler material in the form of particles. The incorporation of selected particulate material in the anticurl layer results in a rougher outer coating surface, which improves processibility (i.e., printer rolls grab the substrate more readily), and prevents "set-off" (i.e., prevents extensive contact between the anticurl layer and an adjacent sheet or substrate). Particles having a particle size than less or equal to the anticurl layer have been found to provide desirable print quality. Any particle may be used in the anticurl layer provided that the particle does not negatively affect the anti-curling properties of the improved substrate. Suitable particles include, but are not limited to, starch particles, polyamide particles, polyethylene particles and aluminum trihydrate particles. Desirably, the particles comprise polyamide particles having a particle size of about 12 to about 50 microns.

The anticurl layer is coated onto the base layer by any conventional coating method including, but not limited to, rod coating, dip coating, spray coating, gravure coating, knife coating, slot coating, nip coating and roller coating. Desirably, the anticurl layer is applied to the base layer by a process wherein the anticurl layer is transferred from a bath onto a roller which extends into the bath, and onto at least one surface of the base layer. The coated base layer then passes under or over a rod, which meters excess coating from the base layer. Once coated, the base layer is dried in a conventional oven or by any other means.

The amount of anticurl layer coated onto a surface of the base layer may vary depending upon the type of base layer used and the application of the final product. For example, a base layer in the form of an uncoated paper may require more anticurl layer coating than a base layer in the form of a coated paper or film due to the increased porosity of the base layer. Desirably, the anticurl layer is applied to a base layer to produce a coating weight of from about 3.0 to about 60.0 g/m^2 of base layer surface area. More desirably, the coating weight is from about 9.0 to about 23.0 g/m^2 of base layer surface area. More desirably, the coating weight is from about 15.0 to about 20.0 g/m^2 of base layer surface area.

The present invention is also directed to an improved substrate having an anticurl layer thereon and a colorant-receiving layer on an opposite side of the base layer. Desirably, the improved substrate of the present invention comprises a colorant-receiving layer as described in U.S. patent application no. 09/058,385, filed on April 9, 1998 and assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference. In one embodiment of the present invention, the improved substrate comprises a base layer, an anticurl layer on a back surface of the base layer, and a colorant-receiving layer comprising hydroxypropyl cellulose, carboxymethyl cellulose,

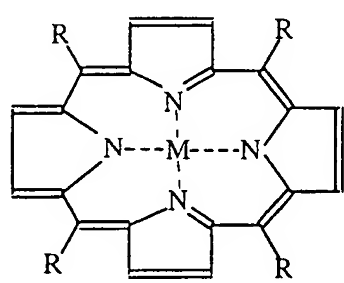
hydroxypropyl-beta-cyclodextrin, and Triton X-100 on a front surface of the base substrate.

The amount of the colorant-receiving layer applied to a surface of the base layer may vary as with the anticurl layer. Similar to the anticurl layer, a base layer in the form of an uncoated paper may require more colorant-receiving layer coating than a base layer in the form of a coated paper or film due to the increased porosity of the base layer. Desirably, the colorant-receiving layer is applied to a base layer to produce a coating weight of from about 3.0 to about 60.0 g/m^2 of base layer surface area. More desirably, the coating weight is from about 9.0 to about 23.0 g/m^2 of base layer surface area. More desirably, the coating weight is from about 15.0 to about 20.0 g/m^2 of base layer surface area. Desirably, the amount of colorant-receiving layer coating applied to the base layer is equal to the amount of anticurl layer coating applied to the base layer.

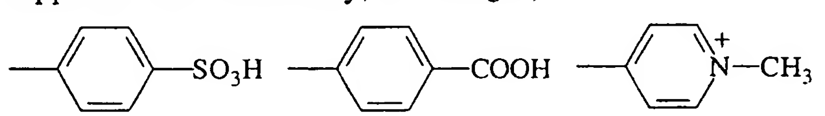
When the improved substrate of the present invention comprises an anticurl layer and a colorant-receiving layer as described above, the improved substrate may be formed by any of the conventional coating methods described above. The anticurl layer may be applied to the base layer first, dried, and followed by the colorant-receiving layer, which is subsequently dried. Alternatively, the colorant-receiving layer may be applied to the base layer first, dried, and followed by the anticurl layer, which is subsequently dried. Desirably, the anticurl layer and colorant-receiving layer are applied to the base layer and dried simultaneously. Care should be taken to avoid contamination of one coating composition with the other coating composition. A particularly suitable method for forming the improved substrate of the present invention comprises a process wherein an anticurl layer is applied to a back surface of the base layer; a colorant-receiving layer is applied to an opposite surface of the base layer; the base layer is passed between upper and lower Meyer rods, which meter

excess coating from both sides of the base layer; and the base layer is dried in a conventional oven.

The improved substrates of the present invention may be used as a print substrate for any colorant or colorant composition. Desirably, the colorant or colorant composition for use with the improved substrates of the present invention comprises a colorant or colorant composition having improved light stability, wherein a colorant stabilizer is associated with the colorant. Such colorant and colorant compositions are disclosed in U.S. Patent Application Serial No. 08/843,410, assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference. More desirably, the colorant or colorant composition contains one or more colorant stabilizers represented by porphines having an extremely short triplet state lifetime. (See e.g., Kubát, et al., Photophysical properties of metal complexes of meso-tetrakis (4-sulphonatophenyl) porphyrin, *J. Photochem. and Photbio. A: Chemistry* 96 (1996), pgs 93-97 which is incorporated herein by reference). Particularly suitable porphines include, but are not limited to, porphines having the following structure:

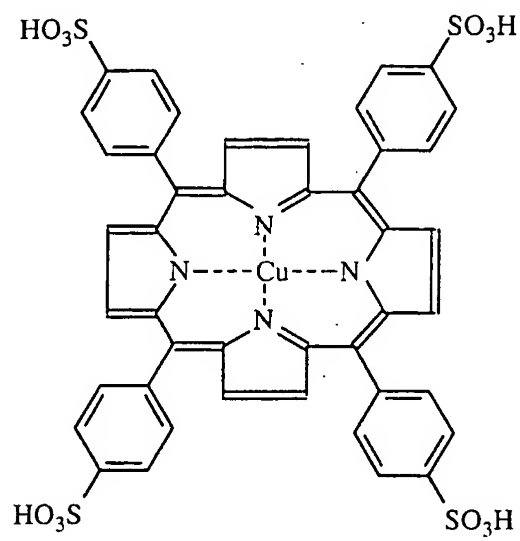


wherein R is any proton-donating moiety and M is cobalt, copper or iron. Desirably, R is SO3H,

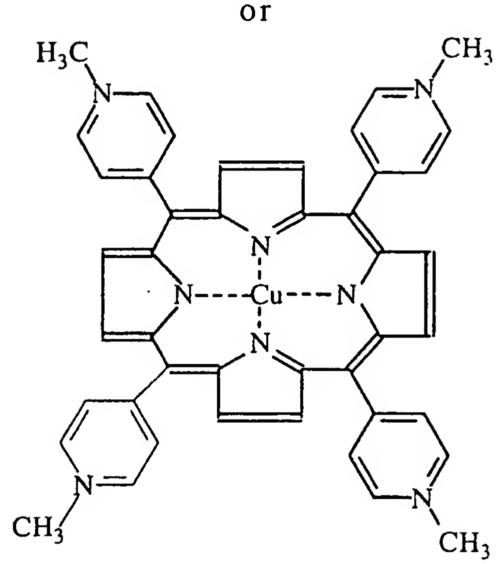


COOH, or R_1COOH wherein R_1 is an alkyl group of from 1 to 6 carbons, or the corresponding salt thereof.

Desirably, the colorant stabilizer is represented by the porphines Cu-meso-tetra-(4-sulfanatophenyl)-porphine (designated CuTPPS4) and Cu-meso-tetra-(N-methyl-4-pyridyl)-porphine (designated CuTMPS4), having the following structure:



or



wherein the copper ion can also be substituted with a cobalt or iron ion. It is also understood that in the case of CuTPPS4,

CoTPPS4 or FeTPPS4, the sulfuric acid moieties may be substituted with salts when in solution, such as sodium salts. The colorant solution may be stabilized with about 0.1% to 10% wt/wt porphine, more preferably about 0.3% to 1% wt/wt porphine, and more preferably about 0.5% wt/wt porphine.

Although not wanting to be limited by the following, it is theorized that the improved substrates of the present invention along with the above stabilizing compounds act by quenching the excited state of a dye molecule by efficiently returning it to a ground state. This reduces the likelihood of an oxidative or other chemical reaction occurring which would render the dye chromophore colorless. The improved substrates of the present invention in combination with the above stabilizing compounds, provide stability to any dye or colorant. A non-limiting list of suitable dyes and colorants are disclosed in U.S. Patent Application Serial No. 08/843,410, assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference.

In addition to the colorant and colorant stabilizer, the colorant compositions applied to the improved substrates of the present invention may also contain additional components, depending upon the application for which it is intended. Examples of such additional components include, but are not limited to, one or more molecular includants; charge carriers; stabilizers against thermal oxidation; viscoelastic properties modifiers; cross-linking agents; plasticizers; charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; fillers such as calcium carbonate, clay and talc; surfactants; buffer/pH adjusters; chelating agents; wetting agents; corrosion inhibitors; biocides; and TINUVIN® compounds; among other additives used by those having ordinary skill in the art. Charge carriers are well known to

those having ordinary skill in the art and typically are polymer-coated metal particles. Desirable surfactants include, but are not limited to, C_{12} to C_{18} surfactants such as cetyl trimethyl ammonium chloride, carboxymethylamylose, and acetylene glycols such as SURFYNOL® 104E. Desirable buffer/pH adjusters include, but are not limited to, borax, hydrochloric acid and sodium hydroxide. Desirable chelating agents include, but are not limited to, EDTA and EDTA complexes or salts. Desirable wetting agents include, but are not limited to, ethylene glycol and glycerine. Desirable corrosion inhibitors include, but are not limited to, a benzotriazole sold under the tradename COBRATEC® 99. Desirable biocides include, but are not limited to, 2,6-dimethyl-m-dioxan-4-ol acetate sold under the tradename GIV-GARD DXN®. TINUVIN® compounds are a class of compounds produced by Ciba-Geigy Corporation, which includes benzophenones, benzotriazoles and hindered amines. Desirable TINUVIN® compounds include, but are not limited to, 2-(2'-hydroxy-3'-*sec*-butyl-5'-*tert*-butylphenyl)-benzotriazole, poly-(N-ß-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate and 2-(2'-hydroxy-3',5'-di*tert* butylphenyl)-5-chloro-benzotriazole. The identities and amounts of such additional components in the colored composition are well known to one of ordinary skill in the art.

The improved substrates of the present invention may also be suitable for use with colored compositions within a carrier. For many applications, the carrier will be a polymer, typically a thermosetting or thermoplastic polymer, with the latter being the more common. Examples of suitable thermosetting and thermoplastic polymers are disclosed in U.S. Patent Application Serial No. 08/843,410, assigned to Kimberly Clark Worldwide, Inc., the entire content of which is hereby incorporated by reference.

The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention.

EXAMPLE 1

An anticurl coating composition was formulated by adding the following components to 1470 parts of deionized water: 25 parts of hydroxypropyl cellulose (Hercules Chemicals), 75 parts of carboxymethyl cellulose (Hercules Chemicals), 42 parts of linear dextrin CLINTON 926™ (ADM, Clinton, Iowa), and 2 parts Triton X-100 (Rohm and Haas). The composition was agitated and heated, as necessary, to obtain a clear solution. The solution was allowed to cool to room temperature before being applied to a substrate.

EXAMPLE 2

The anticurl coating composition of Example 1 was applied onto 7 mil Jen-coat ink-jet photoglossy base sheets using a rod coating method and oven dried. The Meyer rods used were chosen so as to obtain a relatively fixed dry coat weight of about 15 g/m^2.

EXAMPLE 3

The anticurl coating composition of Example 1 was applied onto a 6.2 mil Schoeller paper having a high gloss finish, a face side gel coating and a back side gel coat (Schoeller Paper, designation SN1436). A rod coating method was used so as to obtain a relatively fixed dry coat weight of about 15 g/m^2.

EXAMPLE 4

The anticurl coating composition of Example 1 was applied onto a back surface of Schoeller SN1436 paper and a colorant-receiving composition was coated onto an opposite surface of the paper. A rod coating method was used so as to obtain a relatively fixed dry coat weight of about 15 g/m^2 on both surfaces. The coated paper was subsequently dried in a conventional oven.

Having thus described the invention, numerous changes and modifications thereof will be readily apparent to those having ordinary skill in the art, without departing from the spirit or scope of the invention.

Claims

What is claimed is:

1. An improved substrate for use with colorants comprising a base layer and an anticurl layer on a first surface of the base layer, wherein the anticurl layer comprises one or more polymeric materials.

2. The improved substrate of claim 1, wherein the base layer comprises paper, wood, woven fabric, nonwoven fabric, plastic, glass, metal, or a combination thereof.

3. The improved substrate of claim 2, wherein the base layer comprises a coated or uncoated paper, a film, a paper/film combination or a film/paper/film combination.

4. The improved substrate of claim 3, wherein the base layer comprises a coated or uncoated paper.

5. The improved substrate of claim 3, wherein the base layer comprises a cellulose sheet coated with at least one polyethylene film.

6. The improved substrate of claim 1, wherein the polymeric material comprises polyvinylpyrrolidone, polyvinylalcohol, polyhydroxyethyl acrylate, polyhydroxyethyl methacrylate, polyacrylamide, polymethacrylamide, polyethylene glycol, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, polyacrylic acid and polyacrylic acid salts, polymethacrylic acid and polymethacrylic acid salts, polyvinylsulfonate and polyvinylsulfonate salts, poly-2-acrylamido-2-methylpropanesulfonic acid and poly-2-acrylamido-2-

methylpropanesulfonic acid salts, polyacryloxytrimethylammonium chloride, polymethacryloxytrimethylammonium chloride, polydiallyldimethylammonium chloride or a combination thereof

7. The improved substrate of claim 6, wherein the polymeric material comprises hydroxypropyl cellulose, carboxymethyl cellulose or a combination thereof.

8. The improved substrate of claim 7, wherein the polymeric material comprises a combination of hydroxypropyl cellulose and carboxymethyl cellulose.

9. The improved substrate of claim 1, wherein the anticurl layer further comprises a linear dextrin or a cyclodextrin.

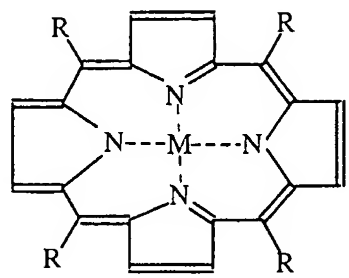
10. The improved substrate of claim 9, wherein the substrate further comprises a colorant-receiving layer on a second surface of the base layer, the second surface being opposite the first surface.

11. The improved substrate of claim 10, wherein the colorant-receiving layer comprises hydroxypropyl cellulose, carboxymethyl cellulose and hydroxypropyl β-cyclodextrin.

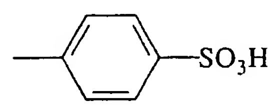
12. The improved substrate of claim 11, further comprising an ink printed onto a surface of the base layer opposite the first surface.

13. The improved substrate of claim 12, wherein the ink contains a colorant stabilizer comprising a porphine.

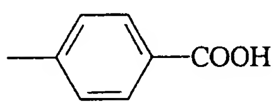
14. The improved substrate of claim 13, wherein the porphine is represented by the following formula



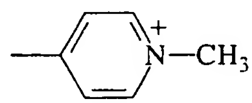
wherein M is cobalt, copper or iron; and wherein R is selected from the group consisting of COOH, CH3COOH, CH_3CH_2COOH, SO_3H,



,



and



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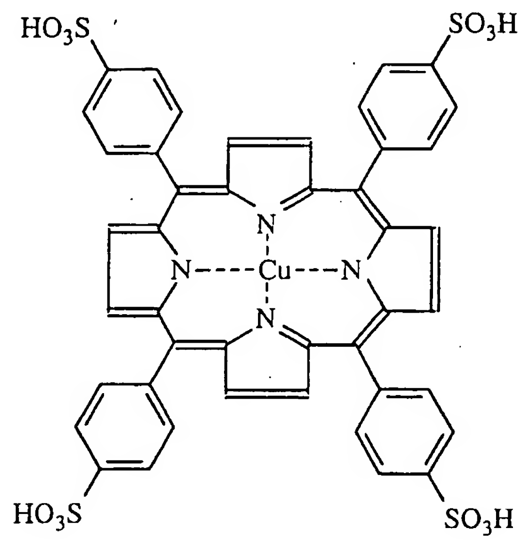
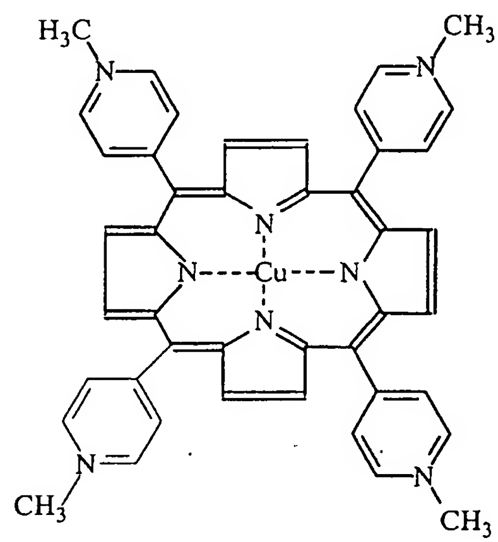
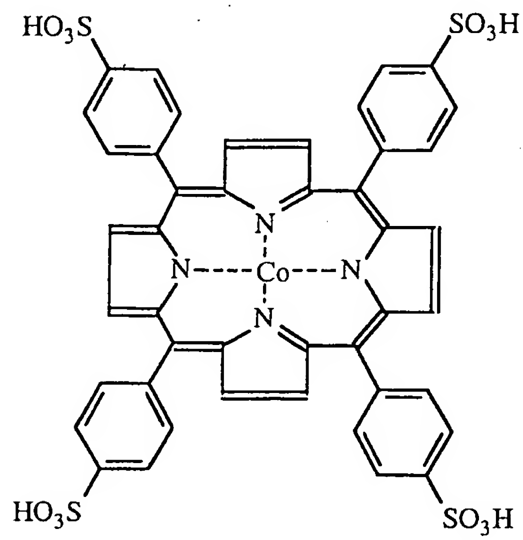
15. The improved substrate of claim 14, wherein the porphine is Cu-meso-tetra-(4-sulfanatophenyl)-porphine or Cu-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



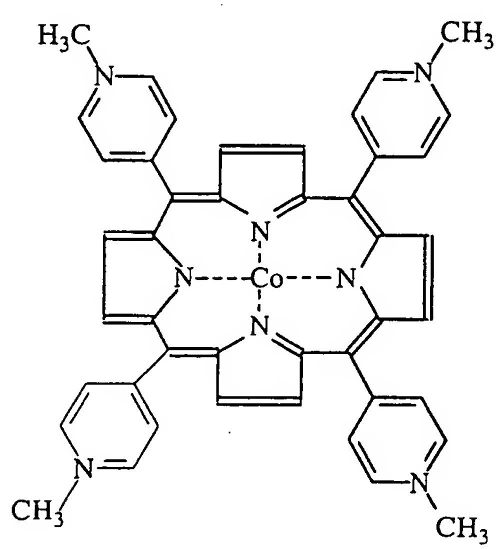
or



or the porphine is Co-meso-tetra-(4-sulfanatophenyl)-porphine or Co-meso-tetra-(N-methyl-4-pyridyl)-porphine, having the following structures, respectively:



or



16. A method of printing comprising:

printing an ink onto a surface of the improved substrate of claim 11.

17. The method of claim 16, wherein the method of printing comprises ink jet printing.

18. An improved substrate for use with colorants comprising a base layer, an anticurl layer, and a colorant-receiving layer opposite the anticurl layer; wherein the anticurl layer and the colorant-receiving layer both comprise hydroxypropyl cellulose and carboxymethyl cellulose.

19. The improved substrate of claim 18, wherein the anticurl layer further comprises a linear dextrin.

20. The improved substrate of claim 18, wherein the colorant-receiving layer further comprises hydroxypropyl β-cyclodextrin.

21. A method of making an improved substrate for use with colorants, said method comprising:

coating a base layer with an anticurl layer, wherein the anticurl layer comprises at least one polymeric material and at least one dextrin.

22. The method of claim 21, wherein the base layer comprises a cellulose sheet coated with a polyethylene film and the anticurl layer comprises hydroxypropyl cellulose, carboxymethyl cellulose and linear dextrin.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/13458

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 469 595 A (XEROX CORPORATION) 5 February 1992 (1992-02-05) claims 1-7,17-19; figure 1; examples 1-3 column 8, line 41 -column 9, line 3 column 9, line 38 - line 44 column 18, line 49 -column 19, line 35 ---	1-7
X	US 5 068 140 A (S.L.MALHOTRA ET AL.) 26 November 1991 (1991-11-26) column 3, line 45 - line 64 column 5, line 1 - line 66 column 6, line 18 - line 57 column 10, line 19 - line 47 claims 1-4,15-17; examples 1-3 --- -/--	1-6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 1999	29/09/1999

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 501 902 A (F.J.KRONZER) 26 March 1996 (1996-03-26) claims 1-3; figures 1,2; example 1 column 3, line 1 - line 18 column 4, line 25 - line 33 column 5, line 35 -column 6, line 14 column 6, line 63 -column 7, line 17	1-6
X	EP 0 737 592 A (MITSUBISHI PAPER MILLS, LIMITED) 16 October 1996 (1996-10-16) claim 1; examples 37,38 page 3, line 10 - line 20 page 5, line 56 - line 57 page 6, line 32 - line 34	1-7
X	EP 0 673 779 A (MITSUBISHI PAPER MILLS, LIMITED) 27 September 1995 (1995-09-27) page 3, line 55 -page 4, line 12 page 8, line 2 - line 8; claims 1,6,10,17	1-6
X	EP 0 605 840 A (MITSUBISHI PAPER MILLS, LIMITED) 13 July 1994 (1994-07-13) page 2, line 40 - line 57; claim 1 page 3, line 1 - line 37 figures 1-3; examples 1,6; table 1	1-6
A	WO 98 23695 A (KIMBERLY-CLARK WORLDWIDE, INC.) 4 June 1998 (1998-06-04) claims 1-73; examples 1,2 page 4, line 16 -page 6, line 18	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/13458

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 469595 A	05-02-1992	US 5277965 A	11-01-1994
		CA 2046572 A,C	02-02-1992
		DE 69113908 D	23-11-1995
		DE 69113908 T	28-03-1996
		JP 2064573 C	24-06-1996
		JP 5096843 A	20-04-1993
		JP 7098418 B	25-10-1995
US 5068140 A	26-11-1991	JP 3114874 A	16-05-1991
US 5501902 A	26-03-1996	CA 2145891 A	29-12-1995
EP 737592 A	16-10-1996	DE 69407574 D	05-02-1998
		EP 0687220 A	20-12-1995
		WO 9420303 A	15-09-1994
		JP 11058932 A	02-03-1999
		JP 10181194 A	07-07-1998
		JP 8503903 T	30-04-1996
		US 5677067 A	14-10-1997
EP 673779 A	27-09-1995	JP 7290818 A	07-11-1995
		US 5882755 A	16-03-1999
EP 605840 A	13-07-1994	JP 7017124 A	20-01-1995
		JP 6191145 A	12-07-1994
		US 5472757 A	05-12-1995
WO 9823695 A	04-06-1998	US 5782963 A	21-07-1998
		US 5855655 A	05-01-1999
		US 5891229 A	06-04-1999
		AU 5589698 A	22-06-1998
		EP 0941293 A	15-09-1999
		ZA 9710689 A	31-07-1998